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# PATENT SPECIFICATION

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## COMPLETE SPECIFICATION

### Granular Tetrafluoroethylene Copolymer Molding Powders

- We, E. I. DU PONT DE NEMOURS AND COMPANY, a corporation organised and existing under the laws of the State of Delaware, United States of America, of Wilmington, State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
- This invention relates to granular tetrafluoroethylene copolymer molding powders.
- The prior art includes many references to tetrafluoroethylene homopolymer and copolymer resins. Polytetrafluoroethylene powders hitherto made available have been of three general kinds. The first two kinds made available were polytetrafluoroethylene granular powders having a total surface area per gram in the range of 1 to 4, e.g., 1.1 to 2.8 square meters, obtained by procedures which comprise polymerizing tetrafluoroethylene in contact with an aqueous medium containing a free radical initiator to obtain a slurry of polymer particles, in non-water-wet form, as disclosed for example, in Brubaker U.S. Patent 2,393,967, issued February 5, 1946; and polytetrafluoroethylene fine powders having a total surface area per gram in the range of 9 to 12, e.g. 10 to 11 square meters, obtained by polymerizing tetrafluoroethylene in an aqueous medium containing a free radical initiator and a telogenically inactive dispersing agent to obtain an aqueous colloidal dispersion of polymer particles, and coagulating the dispersion, as disclosed, for example, in Berry U.S. Patent 2,559,752, issued July 10, 1951, and Lontz U.S. Patent 2,593,583, issued April 4, 1952.
- More recently a third kind of polytetrafluoroethylene molding powder was disclosed Anderson et al. U.S. Patent 3,245,972 having a total surface area of at least 3 and less than 9 square meters per gram, a moldability index of less than 50 and an apparent (bulk) density, indicative of powder flow, of at least 400 g./liter. The method disclosed for preparing this third type of molding powder comprises polymerizing tetrafluoroethylene in contact with a stirred aqueous medium containing a free radical initiator and solid nuclei in the form of agglomerated non-water-wet particles having a total surface area per gram of greater than 3 square meters, characterized in that the medium contains at least  $5 \times 10^{10}$  nuclei per milliliter, polymerization is continued until the particles have a reduced total surface area per gram of less than 9 square meters, and polymerization is discontinued before the total surface area of the particles per gram falls below 3 square meters. The particles so obtained thus have a total surface area per gram of at least 3 and less than 9 square meters.
- The fine powders available have not been suitable for general molding, inasmuch as they tend to crack when preformed and free-sintered in attempts to make massive articles, and inasmuch as they exhibit poor powder flow

properties, which renders them difficult to process in automatic molding machines. Although it has been found possible to minimize the cracking tendency of fine powders by special techniques, as disclosed, for example, in Thomas U.S. Patent 3,010,950, issued November 28, 1961, these techniques further impair the flow properties of the powder. The granular powders on the other hand have usually manifested poor moldability properties, such that relatively high pressures have been required in pressing into preforms which will free-sinter to substantially void-free articles. Again, while it has been found possible by special techniques to improve the moldability of such powders, as disclosed, for example, in Thomas et al. U.S. Patent 2,936,301, issued May 10, 1960, these techniques also impair the flow properties of the powders, so as to make them difficult if not impossible to process on automatic molding machines. Further, while it has been found possible to effect limited improvement in the flow properties of polytetrafluoroethylene powders by special techniques, as disclosed, for example, in Cheney U.S. Patent 2,456,621, issued December 21, 1948, such treatments so impair the moldability of the powders that it has not been possible through their use to convert the highly moldable, poorly flowing powders hitherto made available into powders having a desirable combination of powder flow and moldability properties. Moreover, in general, the special procedures above described for the preparation of highly moldable powders have been considerably more expensive than the procedures required for preparing powders of ordinary moldability properties.

The "long" particles present in granular resins are responsible for decreased powder flow in that these particles occasion bridging. The process of Weisenberger U.S. Patent 3,115,486 describes a process for eliminating bridging, but the latter process also causes shredding in the cut product, which also has an adverse effect on powder flow.

The powders having a total area of at least 3 and less than 9 square meters per gram as prepared are irregular and stringy and hence are water-cut and washed to yield powders having excellent moldability and powder flow.

The present invention provides modified granular fluorocarbon resins which are extremely useful in ram extrusion (ram extrusion is described, for example, in Example I of Cheney U.S. Patent 2,456,621, issued on December 21, 1948) since they comprise particles which are more spheroidal than are the particles of the granular resins. (The term "particle" as used herein refers to an aggregate of the inherent particles formed in the polymerization.) The spheroidal nature of the particles allows better powder flow characteristics, and hence smoother operation in ram extrusion. Thus the expense of cutting the

resin to eliminate or reduce the amount of longs is diminished or eliminated. These resins also exhibit low percent crystallinity.

The resins of the present invention are formed of a copolymer of tetrafluoroethylene and a minor amount (0.003–1.5 mole percent) of a perfluoroethylene unsaturated compound which acts as a modifier to achieve the desired particle size. The modifier is selected from the class consisting of perfluorovinyl compounds of the formula  $CF_2=CF-X$ , wherein X is  $\omega$ -hydroperfluoroalkyl, oxyperfluoroalkyl, oxy- $\omega$ -hydroperfluoroalkyl, and polyether homologues of oxyperfluoroalkyl; and perfluoro-2-methylene-4-methyl-1,3-dioxolane. The particles of the granular polymers of this invention are spheroidal and have an average diameter of from 300 to 1800 microns.

Suitable modifiers (i.e. comonomers) for use in the resins according to the invention are, for example, perfluoromethyl-, perfluoroethyl-, perfluoropropyl-, perfluorobutyl-, and perfluorooctyl perfluorovinyl ether; 2-perfluoropropoxy-perfluoropropyl perfluorovinyl ether; perfluoro-2-methylene-4-methyl-1,3-dioxolane; 1-hydropentafluoropropylene, 2-hydropentafluoropropylene, and 3-hydropentafluoropropylene;  $\omega$ -hydroperfluorobutene-1,  $\omega$ -hydroperfluoropentene-1,  $\omega$ -hydroperfluorohexene-1,  $\omega$ -hydroperfluoroheptene-1, and  $\omega$ -hydroperfluorooctene-1.

The modifiers preferred in this invention are perfluoropropyl perfluorovinyl ether and perfluoro-2-methylene-4-methyl-1,3-dioxolane.

Since the amount of combined modifier required to produce a resin with predominately spheroidal particles is low (0.003–1.5 mole percent), only a minor amount of modifier need be present in the reaction vessel. That amount is dependent on reactivity of the modifier relative to that of tetrafluoroethylene.

The modified resins of this invention can be produced under mild reaction conditions, corresponding, in general, to those described in Brubaker U.S. Patent 2,393,967, issued on February 5, 1946. Thus, generally, an aqueous solution of an initiator and a buffer are introduced into a pressure vessel, as are tetrafluoroethylene and the modifier, and the mixture is heated with stirring at a temperature generally less than 100° C. (preferably 68–75° C.) under elevated pressures of tetrafluoroethylene. A convenient pressure range is several hundred psig.

Since reactivity toward polymerization of modifiers differs from that of tetrafluoroethylene, concentration of the modifier monomer in the monomer mixture must be adjusted in accord with the respective reactivity ratios.

The following test methods were used to determine the physical properties reported in the Examples below. Apparent density was determined by ASTM D-1457-62T.

The term "total surface area per gram," as used herein, refers to a value obtained by

nitrogen adsorption by the procedure described by F. M. Nelson and F. T. Eggertson in *Anal. Chem.* 30, 1387 (1958).

5 The standard specific gravity (SSG) of the resins was determined by ASTM D-1457-62T, except that the specimen was  $1\frac{1}{8}$  inches in diameter rather than 3 inches.

Percent crystallinity is determined as follows. The infrared spectrum of a thin section of an SSG chip is taken. The intensity of the 12.85 micron band is dependent upon the amorphous content of the resin and the intensity of the 4.25 micron band is a measure of sample thickness. An approximation of the percent amorphous content of the resin is obtained by dividing the ratio of the absorbance at 12.85 microns to that at 4.25 microns by about 0.029. The percent crystallinity of the resin is then found by subtracting the amorphous content from 100.

20 The content of combined modifier in the granular resins of this invention was determined by infrared absorbance techniques.

25 The content of combined PPVE (perfluoropropyl perfluorovinyl ether) is the product of 0.67 and the ratio of the infrared absorbance at 10.05 microns to that at 4.25 microns. The data were obtained on cold-pressed films about 0.01 cm. thick.

30 The content of combined perfluoro-2-methylene-4-methyl-1,3-dioxolane is the product of 2.45 and the ratio of the infrared absorbance at 9.96 microns to that at 4.25 microns, obtained on a cold-pressed sample about 0.04 cm. thick.

35 It should be noted that in the various infrared determinations above, the constants are somewhat dependent upon the spectrometer employed.

40 The "percent longs" among the raw polymer particles were determined by the following test. The apparatus consists of a tubular sieve (8 U.S. standard mesh) which is rotated at about 30 rpm. about an axis slightly inclined from the horizontal. Resin is fed to a section of solid tubing attached to the screened section. In the solid tubing, the elongated particles orient themselves parallel to the axis of the screen, and when they slide down over the screen are unable to pass through it. The "rounds" easily pass through the screen. The percentage of particles passing over the screen is reported as percent longs.

55 Powder flow index was determined according to the method reported in Matthews et al. U.S. Patent 3,087,921, issued April 30, 1963, (column 5, lines 5-18); it should be noted, however, that the frequency is correctly expressed as 675 cycles per minute, rather than per second.

60 Wet sieve analysis, a measurement of particle size, was determined according to ASTM D-1457-62T; in the table below  $d_{50}$  is the average particle diameter.

65 Most physical determinations were made on

the raw resin, but standard specific gravity and apparent density measurements were made on "cut" resins. The raw resin is "cut" by the following procedure: 450 grams of resin and 3100 ml. of distilled water were mixed in a Waring Blender at the "fast" speed for 30 seconds. 70

In order that the invention may be better understood, the following detailed examples are given by way of illustration only. All percentages and parts herein are expressed by weight unless otherwise noted. 75

#### EXAMPLES I, II, III, IV.

The modifier employed in these runs was perfluoropropyl perfluorovinyl ether. The reaction vessel employed in these runs was a 5-gallon pressure vessel, vertically disposed, with a stirring shaft along its vertical axis. To the vessel were added 41 pounds of deionized water, 0.931 gram ammonium persulfate initiator, and 13 grams of ammonium carbonate. The vessel was then evacuated and the amount of modifier indicated in the Table was introduced as a liquid. Tetrafluoroethylene was pressured into the vessel and a pressure of 225 psig was maintained during the reaction. The total tetrafluoroethylene introduced was 12 pounds. The reaction temperature was 70° C. and the stirring rate was 780 rpm. The reaction time was 69 minutes for Example I, 89 minutes for Example II, 113 minutes for Example III, 218 minutes for Example IV. The pressure at the end of the run was 40, 75, and 142 psig for Experiments II, III, IV, respectively. Physical data on the resins are reported in the Table. 80 85 90 95 100

#### EXAMPLES V and VI

These examples were conducted in a 2-gallon stainless-steel vertically disposed autoclave, 6 inches in diameter and 16 inches in height, equipped with a four-bladed paddle-type agitator 5 inches in diameter and 1 inch in width. The autoclave was steam-jacketed and a thermocouple measured the temperature which was maintained within  $\pm 1^\circ$  C. 105 110

Into the vessel was charged 5000 ml. of deionized water, 2 ml. of concentrated ammonium hydroxide, and ammonium persulfate initiator (0.23 gram in Example V and 0.46 gram in Example VI). The system was purged three times with tetrafluoroethylene, then liquid perfluoro-2-methylene-4-methyl-1, 3-dioxolane (PMD) was added, 3.8 grams in Example V and 16.5 grams in Example VI. Then 175 psig of tetrafluoroethylene was pressured into the reactor and the reactor was stirred at 750 rpm. at a temperature of 68° C. Total tetrafluoroethylene added was 1680 grams. In both runs the pressure was 50 psig at the end of the reaction. The reaction time was 121 minutes in Example V and 88 minutes in Example VI, and the final pressure in each case was 50 psig. 115 120 125

Physical data on the raw product are found in the Table. The powder flow index was 11.0 and 16.4 grams/second for the raw product of Examples V and VI, respectively.

#### EXAMPLE VII

5 This experiment employed PMD as the modifier, but was run on a larger scale than were Examples V and VI. Into the reaction vessel (the same as that of Example I) was  
10 charged 41 pounds of water, 5 ml. of concentrated ammonium hydroxide, 0.13 gram ammonium persulfate. PMD (50.5 grams) was added. The autoclave was pressured to 175  
15 psig with tetrafluoroethylene, then heated at 90° C. while stirring at 780 rpm. for 62 minutes. The total tetrafluoroethylene used was 12 pounds (5443 grams).

20 The resin of Example VII was then charged to a horizontal  $\frac{1}{4}$ -inch ram extruder. The barrel was maintained at a temperature about 370° C. and the resin was permitted to fall into the loading cavity and forced by a reciprocating ram through the extruder. After the rod

25 passed through the heating zone, it was cooled and solidified before reaching the exit of the extruder as a solid  $\frac{1}{4}$ -inch rod. There was no restriction in the ram extruder to cause back pressure, although, if necessary, a brake could be used on the emerging rod to increase back  
30 pressure within the extruder. The rods thus produced were examined for tensile strength and elongation according to ASTM D-1710-63T.

At a ram extrusion rate of 10 ft./hr., a rod with the following properties was obtained:  
35 tensile strength, 4540 psi; ultimate elongation, 270%. The same resin extruded at 21 ft./hr. had the following properties: tensile strength, 3810 psi; ultimate elongation, 260%.

40 The particles of the products of Examples II to VII are predominantly spheroidal. The value for percent longs for the resins of Example I to VII prepared with varying amounts of modifier was observed to decrease approximately exponentially with increasing percent  
45 by weight of modifier in the total monomer used.

TABLE

## Modified Granular Fluorocarbon Resins

Example	Type <sup>a</sup>	Modifier		Kinetic Molecular Weight ( $\times 10^{-6}$ )	Wet Sieve Analysis (Particle Size of Raw Resin; $\mu$ )			SSG (g/ml)	Surface area (m <sup>2</sup> /g.)	Crystallinity %	Apparent Density (g./l.)
		Wt. % in Reactor	Wt. % in Resin		Mole % in Resin	d <sub>16</sub>	d <sub>50</sub>				
I	PPVE	0.10	0.015	—	0.0056	920	560	220	2.142	2.56	559
II	PPVE	0.18	0.033	—	0.012	840	430	100	2.145	3.36	569
III	PPVE	0.37	0.087	—	0.032	600	350	190	2.131	3.19	503
IV	PPVE	0.92	0.28	—	0.10	550	270	120	2.130	3.68	478
V	PMD	0.22	0.16	7.2	0.065	1360	780	530	2.118	—	523
VI	PMD	0.97	0.75	9.8	0.30	1600	760	360	2.108	—	747
VII	PMD	0.92	0.74	—	0.30	1350	725	390	2.062	—	—

PPVE is perfluoropropyl perfluorovinyl ether, PMD is perfluoro-2-methylene-4-methyl-1,3-dioxolane.

## WHAT WE CLAIM IS:—

1. A granular resin formed of a copolymer of tetrafluoroethylene and from 0.003 to 1.5 mole percent of a perfluoroethylenically unsaturated modifier selected from perfluorovinyl compounds of the formula  $\text{CF}_2=\text{CF}-\text{X}$ , wherein X is  $\omega$ -hydroperfluoroalkyl, oxyperfluoroalkyl, oxy- $\omega$ -hydroperfluoroalkyl, and polyether homologues of oxyperfluoroalkyl; and perfluoro-2-methylene-4-methyl-1,3-dioxolane; the resin predominately consisting of spheroidal particles with an average diameter of 300 to 1800 microns.
2. A resin according to claim 1, wherein the modifier is perfluoropropyl perfluorovinyl ether.
3. A resin according to claim 1, substantially herein described in any of the Examples.

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